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CHEMICAL RELEASE STUDIES IV:
CHEMISTRY OF UPPER ATMOSPHERE RELEASES

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ABSTRACT




Artificial (ionized or unionized) cloud generations in the upper atmosphere are analyzed in terms of two successive processes: first, formation of the initial reaction products and second, evaluation of the non-equilibrium kinetic processes during expansion.

The aluminum-potassium nitrate and the aluminum-barium nitrate reactions are analyzed in detail. Other prospective systems are surveyed.

Models for recombination during expansion of the reaction products are set up.

Methods for improvement of chemical and ionization yield are suggested.



I. INTRODUCTION

For purpose of artificial (ionized or unionized) cloud generation, vapors are released from rocket-borne canisters. These releases are analyzed in terms of two successive processes: First, formation of the initial reaction products and second, evaluation of the non-equilibrium kinetic processes during expansion. Application of various models and comparison with experimental results provides the basis for recommendations for optimization for various types of releases.

Initial reaction product compositions and flame temperatures are calculated on basis of equilibrium processes with the aid of thermodynamical data. This composition, however, is changed during the free expansion of the released matter. Attempts are made to account for the "quenched" composition, primarily the number of free electrons, which survives the expansion process. Ground observations of artificial clouds start usually after the initial expansion process is over.

II. POINT RELEASES (DEFLAGRATION AND DETONATION)

We define a point release as one in which the products of a chemical reaction are dissipated "instantaneously" due to burst of the container. A detonating chemical reaction is characterized by very high rates of reaction and high pressure; a deflagrating or "low" explosive burns more slowly and develops lower pressures.⁽¹⁾

Marmo et al⁽²⁾ used initially the alkali nitrate-aluminum reaction for electron cloud generation. Since no high explosive was added, this method has been analyzed as an equilibrium deflagration reaction. We, therefore, calculate the chemical yield on the basis of the following simple equilibrium model. Passage of the flame front following ignition (which may be rapid) brings the surface of the grains into equilibrium with the hot vapor phase. For simplicity, we neglect heat transfer to the interior of the grains. Since the penetration (i.e., reaction) velocity of the individual grain is assumed to be low, the vapor phase remains in equilibrium with the surface as the temperature and pressure rise.

Preliminary experiments have shown that the aluminum-potassium nitrate reaction is extinguished at low pressures. Therefore we assume that the reaction is quenched when the equilibrium vapor pressure equals the burst pressure of the canister. This accounts for the observed low yield of neutral alkali atoms (chemical yield) in deflagration type releases.

Vapor pressures, flame compositions and flame temperatures for several release conditions are given in the following section. In a typical release, the canister burst pressure was estimated to be 500 atm. The Al/KNO₃ ratio corresponded to Row 3 of Table 1, Section III. From the void volume of the canister, the amount of potassium vapor produced was calculated to be 4.5 moles, or 3% of the total charge (150 moles KNO₃). This is in agreement with the observed chemical yield. From the Saha equation one obtains 3.2×10^{18} electrons/cm³ or 2.3×10^{22} electrons per total charge. The observed number of electrons offer initial expansion was $\sim 10^{21}$ or ~ 25 less than the initial equilibrium ionization value.

Clearly, the chemical yield can be increased by speeding up the reaction rate through the addition of a fast reacting explosive. This was done actually in some releases of the Firefly series.⁽³⁾ However, assuming 100% chemical yield in a detonation, the elevated pressure decreases the equilibrium ionization markedly, and the number of ion-electron pairs is reduced further during expansion of the reaction products. Even minimum second order recombination coefficients of 10^{-12} ion/cm³sec give recombination rates of 10^{19} ion/microsecond. Calculation of recombination loss becomes of critical importance for prediction and optimization of yields. This problem will be treated in Section VI.

III. FLAME TEMPERATURE AND COMPOSITION IN THE ALUMINUM-POTASSIUM NITRATE REACTION

The following is a reprint of a note published in the Journal of Physical Chemistry.⁽⁴⁾

For the purpose of artificial electron cloud generation at high altitudes,² potassium vapors were released from rocket-borne canisters, by the reaction of aluminum powder with potassium nitrate. In order to estimate the number of free electrons in the flame, obtained by ionization of potassium, flame temperatures were calculated for various conditions of release.

The following reaction products are considered to be involved in simultaneous equilibria.^(1,5) $\text{Al}_2\text{O}_3(\text{c})$, $\text{Al}_2\text{O}(\text{g})$, $\text{AlO}(\text{g})$, $\text{O}_2(\text{g})$, and $\text{O}(\text{g})$, where c represents condensed and g gaseous phase. $\text{N}_2(\text{g})$ and $\text{K}(\text{g})$ are assumed to act as inert diluents only. Minor products such as NO , N , K^+ and e^- are neglected in estimating flame composition and temperature. Minimizing, thus, the number of products and assuming ideal gas behavior, the calculation of equilibrium conditions is feasible.⁽⁶⁾ Equilibrium concentrations are calculated in the usual way from the mass balance relations and equilibrium equations. The heat of reaction is then compared with the enthalpy change (from the initial temperature) of the assumed equilibrium products. The temperature at which heat balance is achieved is defined as the flame temperature.

Equilibrium constants were calculated from tabulated free energy functions.^(7,8) The heat of formation of the elements in their standard state at 298.16°K. is taken as zero. For $\text{Al}_2\text{O}_3(\text{c})$ and $\text{Al}_2\text{O}(\text{g})$, $\Delta H_f = -400.1$ and -39.4 kcal./mole, respectively, were adopted.⁽⁵⁾ $\text{AlO}(\text{g})$ is usually present in negligible amounts. For $\text{KNO}_3(\text{c})$ and $\text{O}(\text{g})$, $\Delta H_f = -117.9$ and $+59.16$ kcal./mole were taken, respectively.⁽⁹⁾ Since all alkali nitrates have similar heats of formation and the enthalpies of the gaseous alkalis are alike (except Li)--no great difference is expected in flame temperature and composition by substituting other alkalis for potassium.

Table 1 gives the product composition and flame temperature in KNO_3 -Al mixtures at constant volume (V_c) or constant pressure (P_c). For the constant volume reactions the total pressure (P_t) in the vessel is also calculated. The volume of 165 ml. in Row 1 is the capacity of the canister necessary to hold (without pressing) a mixture of 2 moles of aluminum powder (≈ 200 mesh) and one mole of potassium nitrate (≈ 20 mesh). Row 6 gives the equilibrium conditions at 1 atm. constant pressure. However, preliminary experiments have shown the reaction to be extinguished at atmospheric pressure. In sealed bombs explosions are produced.

According to Table 1, the flame temperature increases with increased pressure in the vessel and decreases with increasing Al/ KNO_3 ratio. The highest (calculated) flame temperatures are obtained in the 2Al: 1 KNO_3 systems -- which is the stoichiometric ratio.

Table 1

APPROXIMATE FLAME COMPOSITION AND TEMPERATURE IN KNO_3 -Al SYSTEMS

Mole Ratio Al/KNO ₃	Reaction Conditions	Flame Composition in Moles ^a					Flame Temp., °K.	
		Al ₂ O ₃ (c)	Al ₂ O(g)	AlO(g)	Al(g)	O ₂ (g)		O(g)
1	V _c = 0.165 l.	0.959	0.039	...	0.002	0.023	0.037	5500
	P _t = 4400 atm.							
2	V _c = 1 l.	.876	.116	0.001	.010	.068	.115	5200
	P _t = 770 atm.							
3	P _c = 500 atm.	.819	.496029	.008	.036	4900
4	P _c = 100 atm.	.848	.145015	.080	.160	4600
5	P _c = 100 atm.	.733	.745044	.002	.003	4000
6	P _c = 1 atm.	.717	.783024	.162	3600

^aIn addition the flame consists also of 1 mole $\text{K}(\text{g})$ and 0.5 mole $\text{N}_2(\text{g})$ per mole of KNO_3 .

As a first approximation, equilibrium electron concentrations are calculated readily from a given flame temperature and the ionization potential of potassium by means of the Saha equation.⁽¹⁰⁾ The number thus calculated, however, is reduced during the expansion of the products, due to recombination processes.

IV. IMPROVEMENT OF ELECTRON YIELD

A. General Consideration

Equilibrium ionization, as a dissociation reaction, may be shown to be a direct function of the temperature and an inverse function of pressure. Since the maximum temperature attainable in an adiabatic chemical reaction is limited by dissociation reactions, the degree of ionization in a given adiabatic reaction is a relatively weak function of the pressure. However, in a flame where the dissociation energy of the combustion products is greater than the ionization energy of a contaminant (Cs in CO and N₂), the degree of ionization is maximized at minimum total pressure. Practical low pressure limits are imposed by the requirements for stable burning and the desired electron concentration and cloud size.

The above qualitative discussion must be examined for a given system in terms of the free energies of reaction. Given cesium as the contaminant of lowest ionization potential, one seeks to maximize the flame temperature by optimum balance between maximum heat of reaction and maximum dissociation energy of the products. For fixed heat of reaction, N₂ and CO are optimum products.

B. High Energy Systems

(1) The Cyanogen-Oxygen-Cesium Flame. Hord and Pennington⁽¹¹⁾ have performed calculations for the (CN)₂-O₂-Cs system. For example,

at a seeding factor $R = \frac{n C_s}{m N_2 + n C_s} = 0.06$ and 1 atm total

pressure, the calculated flame temperature is 4630°K and the number concentration of free electrons (and cations) is $3.5 \times 10^{16}/\text{cm}^3$. This corresponds to an ion yield of 55% per mole of cesium introduced.

Huber and coworkers⁽¹²⁾ at NASA studied the attenuation of microwaves in potassium seeded cyanogen-oxygen flames. Though exact values are not given, it is indicated that the electron concentration at various seeding factors exceeded $10^{15}/\text{cm}^3$.

(2) The Alkali-Halogen System. The most energetic alkali-halogen reaction is that between lithium and fluorine ($\Delta H_{298}^\circ = 146.3$ kcal per mole of lithium fluoride.)⁽³⁾ Since the atomic weight of the elements involved is low, the heat generated per gram of lithium fluoride is also very high. The Li-F system has been considered as a prospective propellant for rocket engines; detailed equilibrium calculations are available.⁽¹³⁾ The other alkali-halogen reactions are not as exothermic as lithium-fluorine on a molar basis. The heat generated per gram of product decreases even more rapidly from lithium fluoride at one extreme to cesium iodide at the other.

The equilibrium ion concentration, however, is not only dependent, on the energy liberated in the reaction, but also on the dissociation potential and the electron affinities of the

elements, upon the ratio of the reactants, and upon the pressure.

Several alkali-halogen systems appear promising for the production of high concentrations of heavy ions. Multi-component systems, such as the combination of a low ionization potential alkali (Cs) with a high bond energy halide (LiF), yield encouragingly large electron concentrations.

Table 2 gives the flame temperatures and compositions of some alkali-halogen systems. It is interesting to note that the mole fraction of ions in the relatively cool cesium-chloride flame is quite large, due mainly to the weak Cs-Cl bond. On the other hand, the flame temperature is not high enough to dissociate the chloride ions into atoms and electrons, hence the low electron concentration. It should be emphasized that the reactants in this case are preheated to 1000°K and, therefore, it is not a true "self-sustaining" reaction. Clearly, a more systematized and detailed analysis of such systems would be of value.

We have attempted also to estimate the electron concentration for a 1 atm lithium-fluorine flame doped with 10 mole% Cs. An exact solution of this three element system is relatively complex for desk calculation. As a rough approximation we assume that in a 10 mole % substitution of Cs for Li the unionized cesium products will distribute in the same proportion as the lithium products (CsF will actually be more highly dissociated) and that the temperature remains the same (it will be lower).

TABLE 2.
Flame Temperature and Composition of Some
Alkali-Halogen Systems

Reactants	M/X Ratio	Temp. of Reactants (°K)	Flame Temp. (°K)	Flame Press. (Atm.)	Flame Composition in Mole Fractions					
					MX	M	X	X ₂	M ⁺	X ⁻ e
Li(l)-F(l)*	1	298	5136	20.4	0.575	0.200	0.202	---	0.017	0.015 0.002
Li(s)-F ₂ (g)	1.25	298	4190	1	0.533	0.289	0.153	---	0.013	0.010 0.003
Cs(g)-Cl ₂ (g)	1	1000	3000	1	0.280	0.307	0.304	0.001 ₅	0.053	0.053 0.000 ₁

* Taken from Ref. (13)

Since the errors tend to cancel, and the doping factor is low, the approximation may be reasonable. The electron concentration is then assumed dependent only on the $\text{Cs} \rightleftharpoons \text{Cs}^+ + \text{e}^-$ equilibrium at 4190°K. We thus estimate $n_e = 1.5 \times 10^{16}/\text{cm}^3$ compared to 5×10^{15} for the pure $(\text{Li} + \text{F}_2)$ reaction. The threefold concentration increase suggests that more careful consideration of this system would be fruitful.

C. Solid Propellant Systems

Although the above systems might conceivably be flown at high altitudes, solid propellant systems have great advantages in weight and reliability. Combinations such as tetracyanoethylene or polymerized cyanogen and alkali superoxides, nitrates or perchlorates can readily be envisaged as analogues of the cyanogen-oxygen system. Less radical systems, closer to present propellant technology, will, of course, require less development, if the highest yields are not sought.

It appears that zirconium and Cs ClO_4 may give a flame temperature of ~5000°K at 100 psi. Organic propellants may be required for proper burning control. A major difficulty anticipated is that of compatibility between Zr and the oxidant. This may be overcome by aluminum coating or alloying with less reactive metals.

Thiokol's TNMA - Al propellant has a calculated flame temperature in excess of 4000°K at 1000 psi. It appears reasonable that reformulated for maximum temperature and minimum pressure and

alkali loading, with Cs NO₃ or Cs N₃ chamber temperatures of ~3500°K will be maintained. At a Cs mole fraction of .05 and 100 psi the electron yield is expected to be ~ 6%.

In summary, propellant type reactions could yield overall efficiencies approaching 50% by utilizing presently known high energy systems to obtain maximum flame temperatures at pressures maintaining electron concentrations below 10¹⁷/cm³. Very respectable equilibrium electron yields may also be obtained by relatively minor optimization of present formulations.

The disadvantage inherent in constant pressure (propellant type) releases of having a long, narrow trail of relatively dilute plasma may be overcome by using a cluster of nozzles, or a large number of nozzles mounted on a spherical container (hedgehog bomb).

V. THE ALUMINUM-BARIUM NITRATE REACTION AND THE "INDIA" RELEASE (FIREFLY 1959)

We wish now to examine the high temperature chemical equilibrium for an alkaline earth system. The "initial states" are shown to be substantially different from the alkali metals -- aluminum analogue. The flame composition of the stoichiometric barium nitrate-aluminum reaction was calculated at two temperatures, viz. 4500 and 3000°K; at constant volume of 231 cm³, corresponding to the volume per reaction weight in the "India" release.⁽³⁾ The reaction products considered are Al₂O₃(c), Al₂O(g), Al(g), O₂(g), O(g), N₂(g), Ba(g), BaO(g) and

BaO(c). The products of the added explosive were ignored.* Free energy functions for BaO(g) were taken from Brewer and Chandrasekharaiah,⁽¹⁴⁾ for BaO(c) from Glassner.⁽¹⁵⁾ Since the thermodynamic functions for the latter are extrapolated from low temperature values, the results given in Table 3. are only approximate.

It is seen that at 3000°K, elementary barium is present in minute amounts, due to the high stability of condensed barium oxide. At 4500°K the gaseous oxide is largely reduced (85%) by aluminum.

The failure to observe elementary barium in the "India" release may be traced to a lower temperature than reported for some of the "Firefly" releases (4500°K), and/or recombination of the products during initial expansion. Since the temperature drops to 3000°K in uniform-density-adiabatic expansion for only 1.5 fold increase in radius (time of the order of 10 μ -sec), it is not an unreasonable assumption that near equilibrium is maintained through this high pressure and temperature region as a result of rapid recombination.

By way of contrast, similar equilibrium calculations for a sodium release reveal no significant decrease in the mole fraction of sodium between 4500 and 3000°K. This is fairly convincing evidence that the failure to observe barium neutrals from "India" is due to

*This is a reasonable assumption, since the most abundant products of the explosive were CO, N₂, and H₂, which at high temperatures do not interact appreciably with other compounds.

TABLE 3.

Flame Composition of the $\text{Ba}(\text{NO}_3)_2$ - Al System

Mole Ratio $\text{Al}/\text{Ba}(\text{NO}_3)_2$	Vol. per Reac. Wt. (cm^3)	Assumed Flame Temp. $^{\circ}\text{K}$	Flame Composition in Moles						
			$\text{Al}_2\text{O}_3(\text{c})$	$\text{Al}_2\text{O}(\text{g})$	$\text{Al}(\text{g})$	$\text{O}_2(\text{g})$	$\text{O}(\text{g})$	$\text{N}_2(\text{g})$	$\text{BaO}(\text{g})$
4	231	3000	1.535	0.440	0.050	1.6×10^{-12}	4.6×10^{-9}	1	0.003
									0.997*
4	231	4500	1.922	0.078	1.05×10^{-5}	5×10^{-5}	6.45×10^{-4}	1	0.845
									-
									0.155*

* At 3000°K the only stable phase considered is $\text{BaO}(\text{c})$; at 4500°K only $\text{BaO}(\text{g})$.

the thermodynamic stability of BaO.

Two approaches may be used to improve the barium releases. First, reductants such as carbon, germanium or zirconium yielding oxides of higher thermodynamic stability may be employed instead of aluminum to obtain more favorable equilibrium distributions. Second, as shown by the various recombination models, low pressure (trail) releases will quench Ba recombination at higher temperatures, thus increasing the atomic barium yield.

We have calculated the equilibrium constants for the reaction $\text{BaO(g)} + \text{C(c)} \rightleftharpoons \text{Ba(g)} + \text{CO(g)}$ at high temperature (Table 4). It is seen that the equilibrium at temperatures $>3000^\circ\text{K}$ is in favor of elementary barium.* Although the reaction rate for graphite may be small, volatile high energy species such as

Table 4.

Equilibrium Constants, $K_p = P_{\text{Ba(g)}} P_{\text{CO(g)}} / P_{\text{BaO(g)}}$,
At Several Temperatures

T°K	3000	3500	4000	4500	4800
Kp	3×10^3	9.5×10^3	2×10^4	4.3×10^4	5.7×10^4

* Note that these results apply to trail releases where flame pressures are relatively low. Under these conditions BaO(g) is assumed to be the stable phase. Its estimated boiling point is 2750°K (Kubaschewski).

$C_2(CN_4)$ may give satisfactory reaction rates. A solid propellant composition containing $Ba(NO_3)_2$, or $Ba ClO_4$ with tetracyanoethylene or polymerized cyanogen, for example, could be utilized. Alternatively, we may seed any high energy composition yielding $CO+N_2$ as products with a thermally unstable barium compound.

For point release detonation charges, similar compositions to the above, incorporating high explosives, offer the possibility that more favorable distributing may be quenched-in during expansion. Since the point release calculations are very complex, such composition are best evaluated experimentally.

VI. RECOMBINATION DURING EXPANSION

We turn now from the consideration of initial equilibrium states to the recombination problem. Given an initial distribution, we wish to analyze the kinetics of the expansion process in order to make reasonable estimates of the final non-equilibrium or quenched distribution. Two models are examined.

A. Elementary Model for Recombination in a Freely Expanding Gas*

The model adopted is based on several simplifications:

a) we assume a temperature and pressure independent second order effective recombination coefficient, since the various recombination mechanisms do not have a very strong temperature or pressure

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dependence.⁽¹⁶⁾ b) The ionization rate is zero at $t > 0$. c) The density is uniform throughout the expanding gas sphere. d) The gas expands spherically with constant radial velocity.

The rate of change of the number of electrons (or cations) per cm^3 , n , is then

$$\frac{dn}{dt} = -\frac{n}{V} \frac{dV}{dt} - \alpha n^2 \quad (1)$$

where the volume $V = 4/3 \pi (r_0 + vt)^3$ at time t ; r_0 is the initial radius, v is the radial expansion velocity, and α is the recombination rate coefficient. This equation is integrated readily:

$$n = 2n_0 r_0^3 / [\alpha n_0 r_0 t (2r_0 + vt) + 2(r_0 + vt)^2] (r_0 + vt) \quad (2)$$

where n_0 is the initial electron concentration.

B. Steady State Model for Recombination in a Nozzle and in a Freely Expanding Gas.

This model has been dealt with in a separate report (Technical Report No. AFCRL 202). It includes the functional dependence of the rate constants, density distribution and expansion velocity. Here we mention only the more important conclusions derived from this treatment.

(1) Minimum electron losses are expected in low pressure releases.

(2) Relatively higher ionization yield may be obtained from small radius containers. Multiple release of small packages will be more efficient than a single large charge.

(3) In an expanded electron cloud the local degree of ionization increases from the edge of the cloud toward the center.

C. Application of the Expansion Models to Past Releases

For the release treated in Section 2, thermochemical calculations indicated that at burst of the canister a gas volume equivalent to a sphere of 12 cm radius (7.2 liter) was formed, containing, as one constituent, 4.33 moles of potassium gas at 4900°K. From the Saha equation we obtain $n_0 = 3.2 \times 10^{18}/\text{cm}^3$ or 2.3×10^{22} electrons for the entire sphere. A recombination rate coefficient of $10^{-12} \text{ cm}^3/\text{sec}$ is adopted.⁽¹⁷⁾ The rate of radial expansion is taken to be the root-mean-square velocity of potassium atoms at the initial temperature, namely $1.8 \times 10^5 \text{ cm/sec.}$, which is in rough agreement with the average velocity obtained from the observed expansion time. The calculated total number of electrons obtained from Eq. (2) by integration over the volume elements is 2×10^{20} , compared to the number obtained from radar returns, namely 10^{21} .

For the "Repeat" release,⁽³⁾ the following results are obtained. Taking the initial fireball temperature to be experimentally determined as 4500°K, we calculate from the loading density (1.6 gr/cm^3) the ideal partial pressure of Cs $\approx 1000 \text{ atm}$ leading to an equilibrium electron yield of 9×10^{22} , roughly twice the value estimated by Gallagher⁽³⁾ from RF returns. (It should be noted that the ionization yield according to Gallagher's estimates is only

2.5×10^{-3} with regard to cesium load.) The initial radius of the fireball is taken as 14.3 cm, corresponding to the volume of the canister.

From the elementary spherical expansion model we obtain the number of electrons quenched $N_{\infty} = 1.1 \times 10^{21}$. From the steady state model $N_{\infty} = 1.44 \times 10^{21}$.

Considering the possibility of an observational error of an order of magnitude and the approximative nature of the calculations, the agreement is encouraging. It should be noted also that initial non-equilibrium ionization may occur at burst, which is not accounted for.

VII. SUMMARY AND CONCLUSIONS

It has been shown by approximate treatment that reasonable prediction of electron cloud yields may be made, for non-detonating systems, by calculation of initial equilibrium distributions and recombination quenching during expansion.

In the aluminum-alkali nitrate reaction maximum ionization is obtained with the stoichiometric reactant ratio.

Propellant type, constant pressure releases have been shown to have potentially greater ionization efficiency than detonation systems. Optimum propellant systems contain contaminants of low ionization potential in flame product gases of maximum thermodynamic stability.

The Cs doped (CO+N₂) carrier provides an absolute optimum for ionization yield.. Solid propellant formulations yielding such optimum products are suggested.

The failure of the India release to yield free barium can be accounted for by the high thermal stability of barium oxide. More powerful reducing agents than aluminum and/or lower pressure releases are suggested to improve the probability of successful release.

Analysis of recombination during expansion by an elementary and a more rigorous steady state model indicates the significance of recombination losses. Minimum electron losses are expected in low pressure releases. In high pressure (detonation type) releases small containers will give relatively higher ionization yields.

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